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Highly oriented δ-Bi_2O_3 thin films stable at room temperature synthesized by reactive magnetron sputtering

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We report the synthesis by reactive magnetron sputtering and structural characterization of highly (111)-oriented thin films of δ–Bi_2O_3. This phase is obtained at a substrate temperature of 150–200 °C in a narrow window of O_2/Ar ratio in the sputtering gas (18%–20%). Transmission electron microscopy and x-ray diffraction reveal a polycrystalline columnar structure with (111) texture. The films are stable from room temperature up to 250 °C in vacuum and 350 °C in ambient air. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4789597]

The development of fast ionic conductors may have substantial societal and environmental impact. Notably, ionic conductors are critical materials in solid oxide fuel cells (SOFC).[1] A conventional SOFC consists of three main components: anode, cathode, and electrolyte; the latter must provide a high ionic conductivity in order to ensure a fast transport of oxygen ions. In present SOFCs, yttria-stabilized zirconia (YSZ) is the most used solid electrolyte, but requires temperatures of 800–1000 °C for reaching a sufficient efficiency. At such high temperature, the life time of a fuel cell is challenged by thermal and chemical degradation, which leads to the need for expensive high-temperature-stable materials.

In response to this challenge, research in the field is focusing on developing new materials with a good ionic conductance at reduced temperatures. In this context, bismuth-oxide based compounds attract attention.[2] Among the six known phases of bismuth oxide (α, β, γ, δ, ε, and η),[3–6] δ-Bi_2O_3 presents the highest known ionic conductivity of any compound, three orders of magnitude larger than β or γ, and two orders of magnitude higher than that of YSZ. Models to explain the high oxide ionic mobility have attributed this effect to a high disorder of oxygen vacancies in the fluorite type structure.[7,8] The main drawback is the very narrow window of stability for the δ phase between 729 and 825 °C, the melting point of bismuth oxide. The stability region of the high-ionic-conductivity phase of bismuth oxide can be extended to lower temperatures by doping the Bi_2O_3 with various elements,[9] especially lanthanides, but this results in a decrease in conductivity of orders of magnitude, a consequence of the increasing order within unoccupied oxygen sites.[10,11] Another way to obtain δ phase at room temperature is epitaxial growth on a single crystal substrate (i.e., epitaxial stabilization of the δ phase)[12] but this is of limited interest for practical applications. Furthermore, a chaotic behavior of conductivity is observed sometime, mostly due to oxygen migration when the stoichiometry is broken.[13] Methods for synthesis of Bi_2O_3 compounds include electrodeposition,[14] chemical vapor deposition,[15] sol-gel methods,[16] and sputtering.[17,18] The last method has the important advantage of operating far from thermodynamic equilibrium, a feature that, in general, enables synthesis of metastable compounds at low temperatures.

In the present communication, we report synthesis of fully (111)-textured thin films of δ-Bi_2O_3 stable from room temperature up to 250 °C in vacuum and 350 °C in ambient air. The films were grown by RF magnetron sputtering in an ultra high vacuum chamber operating at a base pressure of 2.5×10^{-6} Pa. The Bi target (99.99% purity, from Mateck GmbH) was mounted in a water-cooled magnetron having a 45° deviation angle with respect to the axis rotation of the sample. The holder is positioned above the target with a cathode-to-substrate separation distance around 15 cm. The system is described in more detail elsewhere[19,20] The substrates, Si(100) or Al_2O_3(0001) 11×11 mm pieces, were mounted on a molybdenum holder with adjustable rotation speed and heated through a pyrolytic boron nitride heater. Substrate temperature was calibrated prior to deposition by attaching an external thermocouple to an empty substrate and a calibration curve was determined.

The working gas was a mixture of high purity Ar and O_2 with a total flux of mixed gas of 40 standard cubic centimeters per minute (sccm). The O_2 flow/total gas flow ratio was controlled by digital gas flow meters while the total pressure in the deposition chamber during deposition was monitored by a capacitance manometer (Baratron). RF power to the target was applied by a fixed load power supply (Advanced Energy RFX-600). The DC self-bias voltage on the Bi target was constantly monitored. Before each deposition, presputtering of the target in pure argon atmosphere for 10–20 min was performed to remove any surface

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contamination (oxidized layer from previous deposition) on the Bi target surface and 30 min preheating were allowed for stabilizing the substrate temperature.

Phase-pure δ-Bi_2O_3 films were obtained (details below) in a narrow window in deposition-parameter values (oxygen flow ratio 18%–22%, substrate temperatures 150–200 °C, applied power on target 20 W). Fig. 1(a) shows two X-ray diffractograms (XRD) for two as-deposited films on sapphire and silicon substrates. The structure was investigated using Philips diffractometers (Cu Kα radiation) operating at 40 kV and 40 mA. Pole figures were acquired in azimuth angle (Φ) range 0–360° and tilting angle (Ψ) range of 0–90° with steps of 5°.

The structure of our films is substrate-independent despite the large difference between lattice constants (Si—5.43 Å, Al_2O_3—4.78 Å), which excludes the possibility that the films would be epitaxially grown. For phase identification, the peaks around 27° and 58° are the **111** ($2\theta = 27.95°$) and **222** ($2\theta = 57.75°$) peaks for the δ-Bi_2O_3 cubic structure [ICDD PDF 27-0052]. Here, it must be pointed out that the monoclinic α-Bi_2O_3 [ICDD PDF 41-1449] and the tetragonal β-Bi_2O_3 [ICDD PDF 77-5541] phases have peaks close to the above mentioned δ-Bi_2O_3 peaks; α: **012** ($2\theta = 28.0°$) and **024** ($2\theta = 57.9°$); β: **201** ($2\theta = 27.9°$) and **402** ($2\theta = 57.7°$). This can result in ambiguous phase identification, as for example in the claimed synthesis of δ phase in Refs. 17 and 18, where the presented XRD patterns would also be consistent with nanocrystalline α, β, or a combination thereof. Thus, we have performed XRD pole figure analysis (Fig. 1(b)). Φ-Ψ scans were performed for 2θ angles of 28°, 32.4°, and 46.4° corresponding to the **111**, **200**, and **220** peaks, respectively, in the δ-Bi_2O_3 cubic diffraction pattern. Diffraction rings were obtained for Ψ angles of 70°, 54°, and 35° that correspond to the angles between (**111**)^($11\bar{1}$), (**111**)^(**200**), and (**111**)^(**220**) planes, respectively, in cubic δ-Bi_2O_3. These results, which are identical for films deposited on sapphire and silicon substrates, confirm unambiguously that the films have a highly (111)-textured cubic δ-Bi_2O_3 structure.

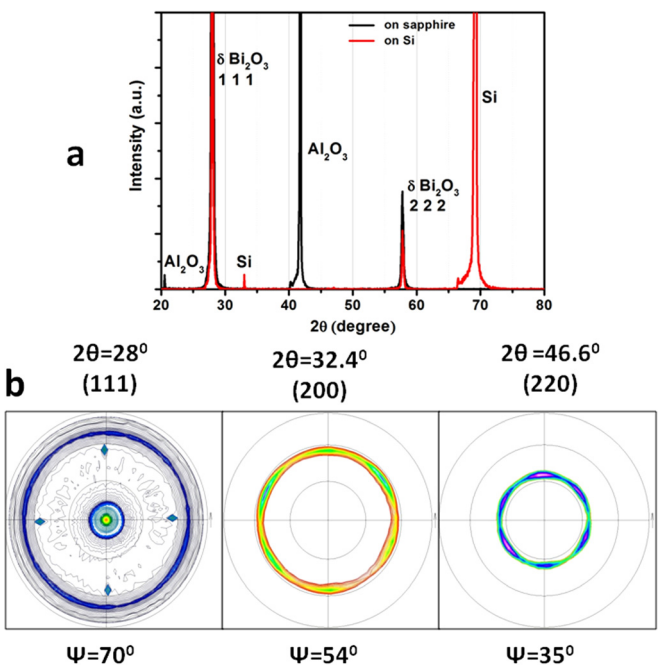

FIG. 1. XRD analysis of δ-Bi_2O_3 thin films. (a) XRD patterns of as deposited films on Si (100) and c-cut sapphire substrates; (b) pole figures for different 2θ angles corresponding to diffraction peaks in δ-Bi_2O_3 phase with observed Ψ positions of diffraction rings.

The structure of δ-Bi_2O_3 films grown on Al_2O_3 substrate was further characterized by analytical high resolution electron microscopy (FEI Tecnai G2 TF20 UT with a field emission gun operated at 200 kV and point resolution of 0.19 nm). The transmission electron microscopy (TEM) specimens were prepared by gluing two slices of samples face to face together, then polishing, dimpling, and finally ion milling to electron transparency. Ion milling was run at 5 keV at an angle of 8° with respect to the surface of the sample and at 2 keV and a lower angle (2°) for the last 10 min. Ion milling was performed with liquid nitrogen cooling of the sample in order to exclude any heating effect on the structure.

TEM bright field and dark field images (Figs. 2(a) and 2(b)) show that the δ-Bi_2O_3 film is uniform and polycrystalline. It has a columnar structure with thickness of 300 nm and ~50 nm column diameter. The selected area electron diffraction pattern shown in Fig. 2(c) demonstrates a strong (**111**) texture in agreement with XRD. This (111) texture can be also observed in the HRTEM image (Fig. 2(d)).

The thermal stability of the δ-Bi_2O_3 films was investigated using a Philips diffractometer (Cu Kα radiation) operating at 45 kV and 40 mA. *In-situ* XRD during annealing (and cool-down) was performed in vacuum at a base pressure of 5×10^{-3} Pa with a heating rate of 30 °C/min. The setup is described in more detail elsewhere.[21] For *ex-situ* experiments in ambient air, the sample was heated under atmospheric conditions (i.e., in a normal tube furnace) using same heating rate, kept 2 h at constant temperature and immediately thereafter the XRD scans were performed. δ-Bi_2O_3 films heated under vacuum conditions are stable up to ~250 °C (Fig. 3, top graph). Above this temperature, a transition to α phase is observed. The same transition occurs for the films annealed under atmospheric conditions but in this

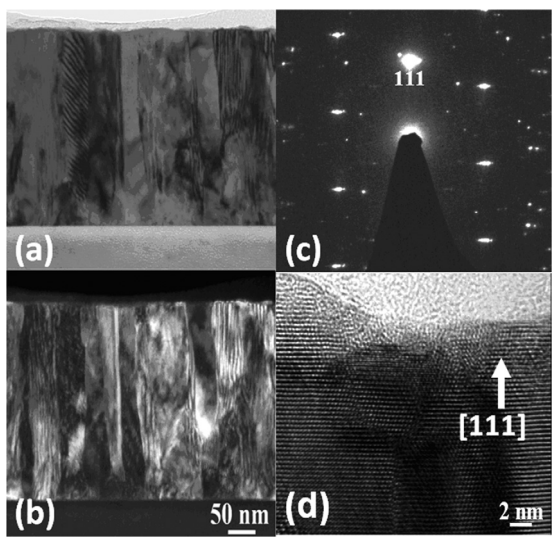

FIG. 2. (a) Bright field TEM image of δ-Bi_2O_3 film grown on Al_2O_3. (b) Dark field image of the same region. (c) Selected electron diffraction pattern of the δ-Bi_2O_3 film. (d) HRTEM image of the δ-Bi_2O_3 film.

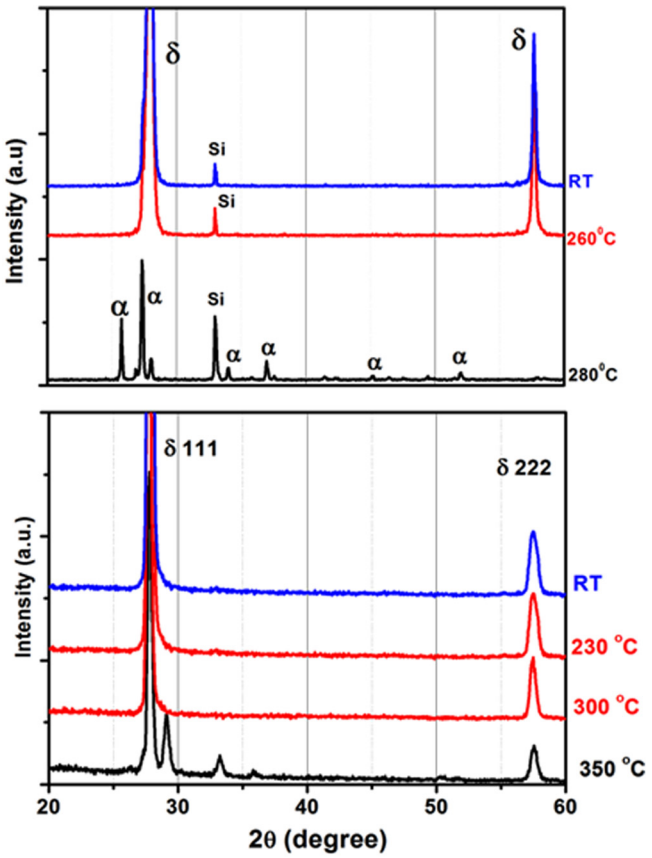

FIG. 3. XRD scans of δ-Bi_2O_3 films (on silicon) annealed at different temperatures. Top: *in-situ* annealing (vacuum); bottom: *ex-situ* annealing (ambient air).

case, it takes place at a higher temperature of ~350 °C, see Fig. 3 (bottom). The process is irreversible, i.e., when the sample is cooled down the bismuth oxide films remain in the α phase.

To explain the formation of the δ-Bi_2O_3 phase, we note two important observations: the narrow window with respect to oxygen flow, and the fact that the thermal stability is higher in air than in vacuum. These observations yield two possible explanations for why the δ-Bi_2O_3 phase forms rather than the thermodynamically stable α phase. The sharpness of the window (18%–22% in oxygen content and, 150–200 °C for substrate temperature) suggests a dynamic competition between the surface kinetics and the thermodynamics of the process. The face-centered cubic stacking in the (111) planes of the cubic fluorite structure is kinetically favored relative to either monoclinic (corresponding to α phase) or rhomboidal (bismuth metal) stacking. The second is related to stoichiometry. This parameter is dependent on the oxygen proportion in the working gas. Since the δ phase can accommodate a degree of vacancies on O sites,[2] it may have increased stability relative to the α phase. These suggested mechanisms are similar to those proposed in the Cr-Al-O system, where an fcc-$(Cr,Al)_2O_3$ phase has been reported in physically vapor deposited films.[22–24] That phase is likely vacancy-stabilized and kinetically favored compared to the more stable corundum phase in the Cr-Al-O system, an observation that supports the suggested mechanisms here. Also, the higher thermal stability in air than in vacuum of δ-Bi_2O_3 films indicates that the presence of oxygen is a key factor in enhancing the stability of cubic δ phase, which in bulk is known to have low stability at lower oxygen partial pressures.[2]

In summary, we have reported synthesis of thin films of δ-Bi_2O_3 by reactive RF magnetron sputtering. There is a narrow window in deposition parameters where these particular films are obtained. Outside this window of operation, other phases or mixtures are obtained. The stability of this highly oriented δ phase from room temperature up to 350 °C may open a new opportunity for possible use as ionic conductor at low temperature.

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